Direct Growth of Si Nanowires on Flexible Organic Substrates

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Abstract A key characteristic of semiconductor nanowires (NWs) is that they grow on any substrate that stands up the growth conditions, paving the way for their use in flexible electronics. We report on the direct growth of crystalline silicon nanowires on polyimide substrates. The Si NWs are grown by plasma-enhanced chemical vapor deposition, which allows the growth to proceed at temperatures low enough to be compatible with plastic substrates (350 °C), where gold or indium are used as growth seeds. In is particularly interesting as the seed not only because it leads to a better NW crystal quality but also because it overcomes a core problem induced by the use of Au in silicon processing, i.e. Au creates deep carrier traps when incorporated in the nanowires.

KEYWORDS Si nanowires, polyimide, flexible electronics, plasma-enhanced chemical vapor deposition.

1. Introduction

Flexible electronics are lightweight, portable, rugged, bendable, rollable, and potentially foldable, for which the market is estimated to be several tens of billions dollars. Applications include wearable systems such as health and environmental sensors, photovoltaics, MEMS and displays. In this rapidly expanding framework, semiconductor nanowires (NWs), in particular crystalline Si NWs, could be integrated in flexible substrates exploiting their unique advantage that they can grow on any substrate that stands up to the growth conditions. This unique advantage is due by the lack of lattice mismatch constrains, which allows direct NWs growth on low-cost [1-3] and/or flexible substrates [4-11]. This, in turn, eliminates the need for complex and time-consuming transferring procedures during which NWs grown on rigid substrates are transferred to arbitrary substrates using soft lithograph, solution-based dispersion, mechanical sliding or printing [12-16]. Up until now silicon NWs have been deposited on flexible substrates like stainless steel [4-7], copper [8-9], and aluminum [10] foils and carbon-fibers [11], exploiting the vapor-liquid-solid (VLS) mechanism using foreign metals as growth seeds. However, direct growth of Si NWs on polymer substrates has not been reported to date, despite their low-cost, scalability and easy manufacturing within the Si technology platform. Process compatibility with silicon fabrication technology requires that polymeric substrates be used at relatively low temperatures (<400 °C). This is in contrast to the reports cited above which use of higher temperatures (460 °C and above) that favor the VLS mechanism and the growth of crystalline NWs. This work addresses these shortcomings in the in the literature.

As mentioned above, the VLS mechanism requires the use of a metal seed to induce and dictate the NW growth, where gold is the most commonly used. The properties that make Au the most universal material for NW growth are discussed in the literature [17]. However, Au is a deep carrier trap in silicon and deteriorates the electronic properties of Si NWs if incorporated in the NW body. For this reason Au should be avoided in Si-based device fabrication. Active research is ongoing to find alternative metals that can induce the NW growth. Among others, In has shown to be a possible choice to grow Si NWs [18-20]. Owing to its low-melting T (157°C), indium endows polymer-compatible deposition environment. Indeed, high density of Si NWs has been obtained at growth temperatures down to 330 °C [20] on Si substrates. If incorporated in Si, In behaves as a shallow acceptor, hence, is much more electronically favorable than Au as growth seed.

In this work, we report the direct growth of Si NWs on polyimide substrates by the VLS method. The metal-assisted growth has been achieved at 350 °C using plasma-enhanced chemical vapor deposition (PECVD), where both In and Au have been used. Although our main goal was to use In, the high efficiency of gold as NW seed [17] was exploited to set the most appropriate growth conditions on polyimide substrates, albeit important differences were observed in some growth aspects between the two metal seeds. This work shows that a high density of crystalline Si NWs can be grown on a flexible plastic film, after peeling off polyimide film from its rigid support during growth. Despite the low growth temperature, an accurate control of the growth parameters has allowed us to obtain good crystalline quality of Si NWs, which exhibit better quality when grown using In seeds.

Si NWs have been integrated in plastic supports via post-growth transfer onto appropriate substrates. Techniques such as dry transfer [21], contact printing [22] and spray-coating [23] have been suggested and gas- [21] and bio-[24] sensors have been fabricated using some of those methods. The direct growth on plastic, as proposed in the present manuscript, requires less technology steps to be implemented into devices, offering in principle similar performance. As an example, very high gas sensitivity can indeed be obtained with the fabrication of on-chip devices that make use of as-grown Si NWs [25]. Moreover, other

types of devices, e.g. NW-based photovoltaic cells [2, 6] or lithium ion batteries [11], are generally fabricated using as grown material. Our growth method indicates that they can be realized on plastic substrates, paving the way for flexible devices based on those architectures.

2. Experimental section.

The growth of Si NWs was carried out by PECVD with a gas mixture of SiH_4/H_2 on a stack of Si/SiO_2/polyimide/(*a*-Si)/In (or Au) substrate. A 4-8μm thick polyimide (PI-2611, HD MicroSystems) layer was spin-coated on the thermally grown SiO_2 layer of Si substrates. This was followed in some cases (see below the description of the results) by the deposition of a thin amorphous Si (a-Si, 50-100 nm) layer by PECVD subsequently covered by Au (2nm) or In (4-10nm) films via e-beam evaporation. SiH_4/H_2 mixtures with 1:5/1:20 dilutions were used at a total pressure of 1 Torr and a plasma power of 5 W. The growth was carried out at 350 °C for 10 minutes. The morphology and density of the NWs were studied by scanning electron microscopy (SEM, Zeiss EVO MA10, acceleration voltage: 5 kV) while their crystal quality was charachterized by transmission electron microscopy (TEM). For TEM analysis, the nanowires were mechanically scrapped onto a holey carbon grid followed by imaging in a Jeol 2100F FEG TEM operating at 200 keV.

After growth, the polyimide layer with the on-grown NWs could be easily detached from the supporting substrate. Different polyimide thicknesses did not result in any significant difference in the NW yield and morphology, thus indicating a reproducible growth temperature at the polyimide surface.

3. Results and discussion

We have grown Au- and In- induced silicon NWs on polyimide layers deposited on Si substrates, using Au or In nanoparticles to induce the growth. The polyimide layer was peeled off the Si substrate after growth to obtain a flexible mat of Si NWs.The supporting substrate can then re-used for further growths. In the following we discuss the density, morphology and the crystal structure of the NWs obtained with our growth procedure.

3.1. Nanowire density and morphology

3.1.1. Au-induced Si NWs. Although Au is an efficient growth seed, its interaction with the substrate is important to the growth success. The direct growth on polyimide requires indeed a careful treatment of the substrate to obtain dense and long NWs. This aspect is pointed out in Figure 1(a), where we show the SEM micrographs of the growth of Au-seeded NWs for Au deposited directly onto the polyimide film. Almost no wire was obtained. The important role played by the substrate is demonstrated in Figure 1(b), where we report the result obtained in the same growth but on a Si substrate placed adjacent to the polyimide: a high density of oriented Si NWs was achieved. Colli et al. [26] have shown that the interaction between Au nanoparticles and the Si substrate leads to the formation of AuSi intermetallic compounds that facilitate the Si supersaturation in the nanoparticle and hence the NW nucleation. Therefore, to favor the growth on polyimide, we have deposited a thin (50 nm) a-Si layer on the top of polyimide. Figure 1(c) shows that the method is successful because, under the same growth conditions, the NW density increases. The density can be of course increased by increasing the silane partial pressure, see figure 1(d), but the reached density is still not satisfactory. A further increase of the SiH_4 partial pressure would increase the deposition rate, which adversely affects the NW crystallinity and lead to a higher amount of parasitic growth [20, 24].

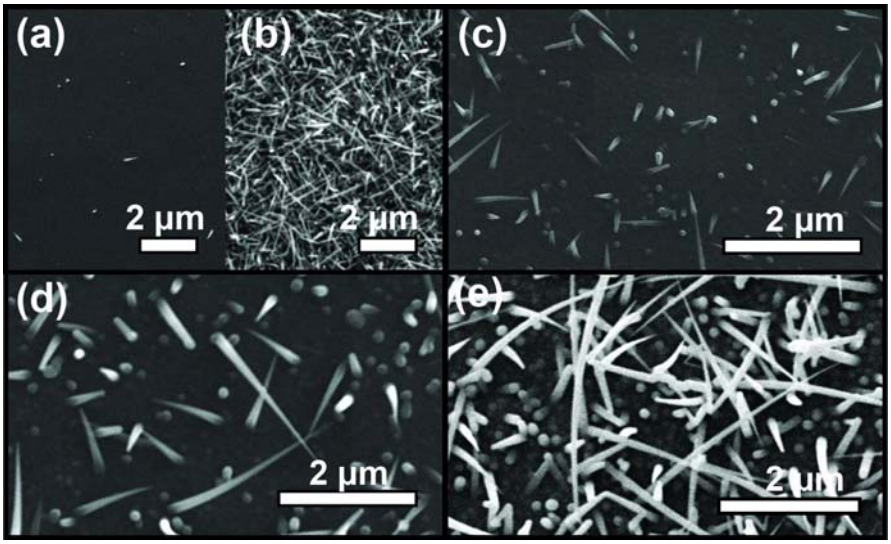

Figure 1. SEM plan-view images of Au-seeded Si NWs. (a) Growth on polyimide; (b) growth on Si (100) using the same growth conditions as in (a); (c) Growth on a 50 nm thick amorphous Si layer deposited on polyimide; (d) same as in (c) but with increased SiH_4 partial pressure, from 91 mTorr (c) to 167 mTorr (d); (e) same growth conditions as in (d) but after H_2 pre-treatment of the substrate.

We have instead used a pre-treatment of the Si/SiO_2/polyimide/*a*-Si/Au substrate in H_2 plasma that has been shown to be useful to the NW growth at low temperatures [26]. The results are reported in figure 1(e): a treatment in H_2 plasma at 350 °C for 10 minutes increases the NW density with respect to the sample grown under the same parameters, but without a plasma pre-treatment (figure 1(d); notice that this image is tilted by 60° that increases the apparent density). Note that silane is introduced into the growth chamber without interrupting the plasma.

We have then investigated how the a-Si thickness on the growth. Figure 2 illustrates the effect of the a-Si thickness on the NW yield in the presence of H_2 plasma pre-treatment. Only a few wires were observed in the sample where Au was deposited directly onto polyimide (Figure 2(a)). This confirms the poor effectiveness of Au as seed if directly deposited on polyimide. As expected, the NW density increases with a 50 nm thick layer of a-Si on polyimide and even more for a 100 nm thick a-Si layer (Figure 2(c)). The length of the NWs after 10 minutes growth exceeds 3 µm and NWs are slightly tapered. Au nanoparticles (NPs) are generally observed at the NW tip.

In brief, it is possible to obtain high density of Au-induced Si NWs on polyimide at 350 °C combining an a-Si layer deposited on polyimide prior to Au deposition and a pre-treatment of the substrate in H_2 plasma at the growth temperature. Both processes make possible (a-Si layer) or easier (plasma) the formation of AuSi NPs *before* growth starts via the interaction of Au and the a-Si layer, which accelerates the supersaturation of the seeding NPs. Without these processes, the high PECVD growth rate leads to the growth of a thick parasitic layer able to bury the Au NPs before NW nucleation occurs.

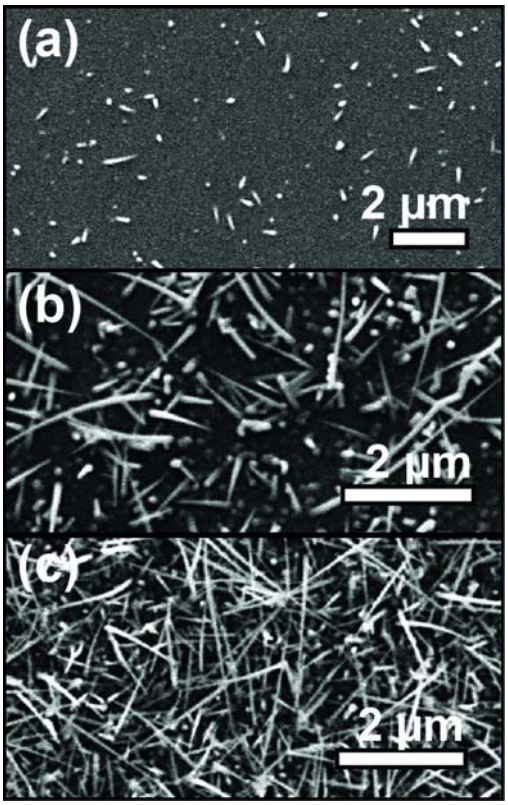

Figure 2. SEM images of Au seeded NWs with different a-Si layer thickness: (a) 0 nm; (b) 50 nm; (c) 100 nm. All substrates were pretreated with H_2 plasma.

3.1.2. In-induced Si NWs. The substitution of gold in the growth of Si NWs is of critical importance where In offers an excellent alternative. However, the use of In as growth seed is coupled with one important issue, i.e. the oxidation of the In NP surface renders In inactive for the growth. The oxidation occurs during the transfer of the substrates from the metal-deposition chamber to the growth chamber. This work shows that once this issue is addressed, the growth rate of In-induced NWs does not vary significantly from that of Au-induced NWs, in line with recent reports on In-induced NWs grown on other substrates [18-20].

Figure 3 shows the results of In-induced NWs growth. Figure 3(a) suggests that if In is simply deposited on polyimide without further treatments, only a few NWs are grown. A chemical etch in buffered HF proved to be unsuitable because the etch removes In from the polyimide layer. A larger, but still unsatisfactory, NW density is achieved if a 50 nm thin a-Si layer is deposited on polyimide prior to In deposition (Figure 3(b)), similar to that of Au seeds. A much higher density is obtained providing a pre-treatment in H_2 plasma is performed right before the growth (Figure 3 (c)). Note that silane is introduced into the growth chamber without interrupting the plasma.

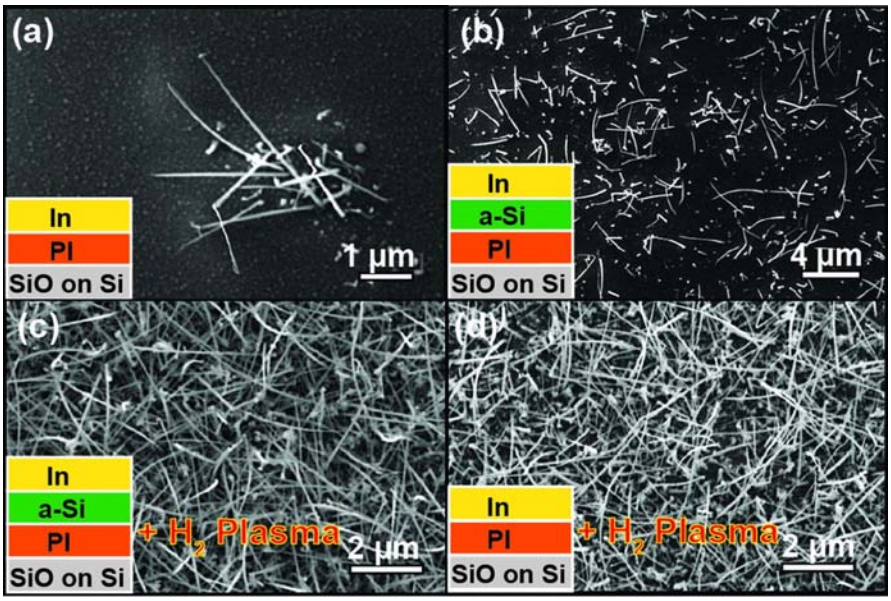

Figure 3. SEM images of In-seeded Si NWs. (a) In nanoparticles are formed on polyimide without any treatment; (b) In is deposited on a thin a-Si layer deposited on polyimide; (c) In NPs are formed directly on polyimide and treated with H_2 plasma before growth; (d) same as in (c) but with a thin a-Si layer deposited on polyimide.

In contrast to what observed with Au seeds, the presence of the a-Si layer is not necessary to achieve a high density of NWs for In seeds. The use of H_2 plasma treatment of In NPs formed directly onto the polyimide is sufficient to obtain a high density NWs, as shown in Figure 3 (d). H_2 plasma has a strong reductive effect making In NPs available for growth directly on polyimide. Under the same growth conditions, In-induced NWs appear to be slightly longer than those grown using Au-seeds. This indicates that the In NPs become very active as soon as the surface oxide formed during substrate preparation is removed, as confirmed by the observation of In NPs at the final end of the Si NWs (Figure 4).
In brief, a high density of Si NWs can be obtained using In seed formed directly on polyimide without resorting to an a-Si layer on polyimide.

3.2. Study of the Si NWs structure.
SEM results indicate that for both Au and In seeds the presence of a metallic nanoparticle is observed around the NW tip region. Figure 4 shows the TEM results of NW tips for In- (a and b) and Au- (c) seeded NWs. Figure 4a is a many-beam bright-field image of the In NW tip while Figure 4b is the In-M edge energy filtered chemical map, showing the distribution of In. The In seed is present along the NW sidewalls and suggests that the In-seeded growth occurs with a liquid nanoparticle. In contrast the bright-field image of the Au seeded NW (Figure 4c) shows that the nanoparticle is present at the NW tip.
As will be shown below despite the low growth temperature and the lack of any crystalline substrate, the Si NWs show a high degree of crystallinity with little or no lateral growth of amorphous Si on the sidewalls. This is particularly important for the deposition of electrical contacts on the top of the sample. A further interesting aspect is that we have observed important differences in the crystal structure of the NWs grown with different seeds.

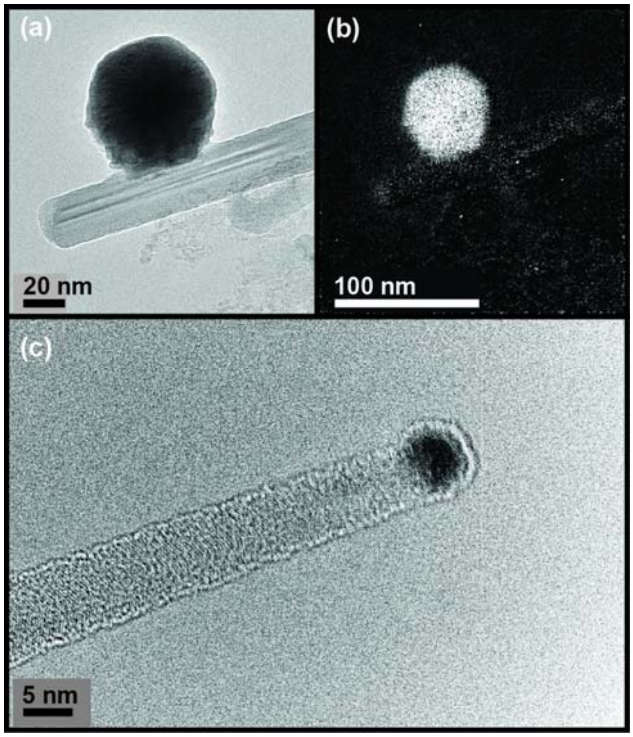

Figure 4. TEM mages of NW tip region. (a) bright-field image of an In-induced Si NW; (b) corresponding In chemical map obtained using energy filtered TEM; (c) bright-field image of a Au-induced Si NW.

Figure 5 shows a high-resolution TEM image of a representative Au-seeded Si-NW (Figure 5(a)) and the fast Fourier transform (FFT) pattern of that image (Figure 5 (b)). The sharp spots in the FFT confirm the NW crystallinity with a diamond cubic crystal structure and stacking faults visible as streaks between the Bragg spots (Figure 5 b). The NW growth direction is along <110>. The NW sidewalls of the wire show a thin layer of amorphous material, which could be due to native oxide formed in air after growth or amorphous-Si formed during the growth stage. A thin amorphous layer is present in the In-seeded nanowires as well.

In general In-induced NWs show a smaller number of defects compared to Au-induced NWs. Moreover, lattice structures, which suggest the presence of both lonsdaleite (a hexagonal phase of group IV materials) and diamond cubic phases, were observed In-induced NWs only.

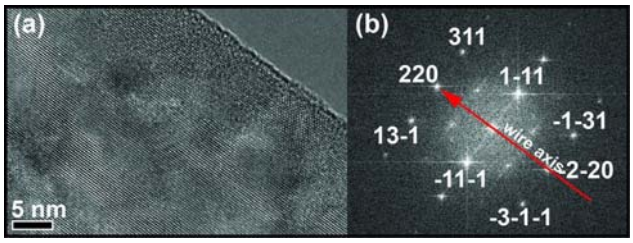

Figure 5. (a) TEM image of a representative Au-seeded NW. (b) fast Fourier transform (FFT) pattern of the image.

Figure 6(a) shows a high resolution TEM image of part of an In-induced NW. The FFT pattern of the image is reported in Figure 6(b), which could correspond to a lonsdaleite structure with <0002> growth direction. The lattice constants a=4.06 Å and c=6.6 Å, extracted from Figure 6(b), agree very well with those reported by Fontcuberta i Morral et al. [27] in Si NWs grown using standard chemical vapor deposition at growth temperatures above 500 °C. Those values, however, are different from those reported for 2H Si NW shells where the hexagonal structure was epitaxially imposed by the GaP core [28, 29]. Studies carried out elsewhere [30-32] show that "anomalous" diffraction patterns could arise from defects of the cubic structure, giving rise to apparent hexagonal patterns due to superposition of different crystal regions. It is worth pointing out that the measured angle between directions indexed as $[10\bar{1}1]$ and $[10\bar{1}\bar{1}]$ in Figure 6(b) is 56°. In particular, Kohno [30] and Den Hertog [32] have attributed similar patterns to double diffraction by {111} twin planes observed from [123] and [321] directions in cubic structures.

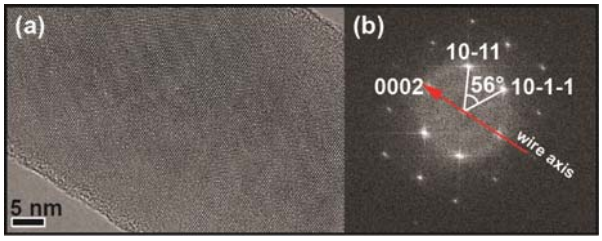

Figure 6. (a) TEM image of an In-seeded NWs. (b) fast Fourer transform (FFT) pattern of the image.

4. Conclusions

We have shown the direct growth of silicon nanowires on a plastic, flexible material such as polyimide, which is a typical component of organic electronics. This was achieved exploiting the potential for plasma-enhanced chemical vapor deposition to grow NWs at low temperature. The Si NWs were grown at 350 °C, a temperature which does not alter polyimide characteristics. Both Au and In were used as metal seeds to induce the NW growth. In both cases, the simple metal deposition on polyimide is not sufficient to achieve high NW density. To induce Au-seeded NW growth, the deposition of a thin (100 nm) amorphous silicon layer on the plastic material is essential to favor the formation of AuSi nanoparticles. Likewise, the removal of indium oxide by H_2 plasma is necessary to induce the In-seeded growth directly onto polyimide substrates.

The success of the In-induced growth on plastics is of particular importance because it overcomes one of the major drawbacks of gold, i.e. when incorporated in any fabrication step, Au can create deep carrier traps, therefore, must be avoided in the silicon technology platform. This paper demonstrates that good crystallinity Si NWs can be grown on an amorphous plastic substrate at temperature as low as 350 °C. The In-induced Si NWs were shown to exhibit a superior crystal quality compared to that of Au-induced NWs. TEM analysis indicates that a lonsdaleite phase is only observed in the In-induced NWs (not in Au-induced NWs). In contrast, only a cubic structure was observed in the Au-seeded NWs. Further studies are currently in hand to confirm these findings and to understand the role of In in the formation of the lonsdaleite phase and to control the direction of growth.

The amorphous nature of polyimide can explain the disordered orientation of the NW growth. Work is in progress to achieve some degree of ordering. However it is worth noting that several devices (photovoltaic cells and sensors) have been reported to use disordered Si NWs [2, 6, 11, 21] for operation. Some of those devices [21] display a good performance precisely because they exploit the disordered nature of the grown NWs. This paper offers the opportunity to develop a low-cost platform, where our results clearly indicate a direction towards a sustainable use of Si NWs. Indeed, this work uses fewer and simple process steps, demonstrating that Si NWs can be directly processed on flexible substrates using low-cost materials and inexpensive growth methods.

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